HIGH TEMPERATURE THERMOCOUPLE RESEARCH AND DEVELOPMENT PROGRAM

MONTHLY PROGRESS REPORT NUMBER 6
Period 1 November 1963 to 1 December 1963
Contract Number NAS 8-5438
Request Number TP 3-83547

prepared for
GEORGE C. MARSHALL SPACE FLIGHT CENTER
Huntsville, Alabama

work performed by
AUTO-CONTROL LABORATORIES, INC.
5251 West Imperial Highway
Los Angeles, California 90045

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Prepared By: [signature]
Section Head, Environmental Components

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ABSTRACT

This report covers the period 1 November 1963 to 1 December 1963, under Contract NAS 8-5438, which calls for twelve months of research and development of a high temperature thermocouple capable of measuring rocket engine exhaust temperatures in the 3000°C range, under adverse conditions of oxidation, erosion, vibration and shock.

The primary objectives of the program are to advance the state-of-the-art of high temperature thermometry, and to develop an end product suitable for in-flight temperature measurements on the SATURN vehicle.

Work during the current reporting period was directed principally to consolidation of research data concerning oxidation resistant coatings and high temperature reactions of materials being used, or considered for use in this project. Results are tabulated herein.

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SECTION I

SUMMARY

1.0 Period Covered

This report covers the period 1 November 1963 to 1 December 1963.

1.1 Statement of Work

The Contractor shall advance the state-of-the-art of high temperature thermometry and specifically improve the technique of accurately measuring high temperatures by designing, fabricating, testing, and delivering nine (9) thermocouple probes capable of operation in the 3000°C temperature range under adverse conditions of erosion, oxidations and high stress levels for useful periods of time. Also, present methods of thermocouple probe fabrication will be modified such that the end product will be suitable for in-flight temperature measurements on the SATURN vehicle.

To accomplish the above objectives, the Contractor shall consider and explore specific R&D efforts as follows:

a. Development of the physical structure of an immersed probe to attain minimum drag and highest resistance to bending and shear forces.

b. Ascertain the best combination of ingredients in the protective coating of the probe to extend the term of oxidation resistance.

c. Determine the best combination of compensated lead wires for use with the immersion type probes.

d. Incorporate latest state-of-the-art materials as potting and sealing elements in the base of the probe.

1.1 Statement of Work Cont....

e. Determine effects of reactions between oxide coatings and tungsten in relation to the emf output.

f. Establishment of rates of erosion for different types of refractory coatings such as tungsten disilicide, carbides and cermets when subjected to high velocity, high temperature gas streams.

1.2 Progress

Accomplished during the current reporting period were:

a. Analysis, Form and Shock Drag

An analysis performed on hypothetical gauges of the same general type as the Type 4735 gauge, revealed the possibility of extremely high shock loadings if the gauge is mounted transverse to flow.

b. Oxidation Resistant Coatings

A summary of research done to date on various types of coatings was made, and the results were tabulated.

c. High Temperature Reactions

Results of studies performed to date on high temperature reactions applicable to this program were summarized and tabulated.

d. Tests

Tests of lead wires and materials were continued.

SECTION II

PAST PROGRESS

2.0 General

Previous effort was reported in ACL Progress Reports T-1097-1 through T-1097-5.

2.1 Prototype Design and Development

As was previously reported, objectives for the first prototypes were limited to the 4000°F - 4500°F range in the interest of accumulating test data for analysis, the results to be utilized in future design.

A design approach for the prototype gauges was selected, and drawings prepared, detailing means of fabrication and assembly.

Investigations made into fabrication techniques involved in working vapor deposited Tungsten, resulted in improved material handling techniques.

Shock and vibration tests, performed on a prototype mock-up, resulted in a conclusion that the sheath material was intrinsically capable of withstanding the specified shock and vibration requirements.

Samples of various types of compensation lead wires were ordered for test and evaluation.

An evaluation of the SRI calibration tests for ACL Type 4734 gauges was made, resulting in a conclusion that an optimum immersion depth might be in the order of 1-1/2 inches in an isothermal region.

The two Type 4734 gauges tested by N.A.S.A., and returned to ACL were examined, and results of the examination were reported.

2.1 Prototype Design and Development Cont....

A test of a "no-insulation" approach was started, but was aborted due to a failure in the test oven.

Three prototype gauges were delivered to M-ASTR-I, on 17 October 1963, for test and evaluation. Calibrations of this type of gauge indicated a shift in emf output to a higher value than that shown in previous calibrations. The shift was believed due to a spurious emf contributed by the "compensated" lead wires. The curves, however, paralleled the curves taken by Southern Research Institute, as well as those predicted by ACL.

SECTION III

CURRENT PROGRESS

3.0 General

Effort during the current reporting period was devoted principally to research of latest available literature, and preliminary design of the second generation gauges. Information received from N.A.S.A. regarding performance of the first generation prototypes, as well as other information requested regarding installation and use, were not received in time for incorporation in current works. It is assumed that such information will be made available in the near future.

3.1 Progress

3.1.1 Analysis, Aerodynamic Loading

All information, regarding the medium in which the gauges will run, has not been received. Therefore, a definitive analysis is not possible. A general assessment can be made, however, of the effects of aerodynamic loading, in arbitrary terms. The general geometry of the Type 4735 prototype gauges was used in preparing the estimates of form drag and shock drag shown in Figures 1 and 2, respectively.

3.1.1.1 Form Drag

The form drag was calculated for a projected area of 2.36×10^{-3} ft.^{2}, medium velocity to 5000 ft/sec, and medium densities of 2.045×10^{-3}, 2.37×10^{-3} and 3.567×10^{-3} slugs per ft.^{3}. The curves are shown in Figure 1, with maxima from 55 pounds to 95 pounds. An immersion depth of 1.8 inches was hypothesized. These curves take the usual shape associated with form drag. A drag coefficient of 0.9 was used in all computations. The loads thus indicated did not account for failures seen in tests of other gauges of a similar type. Therefore it was suspected that a shock condition may have existed.

3.1.1.2 Shock Drag

To obtain an estimate of shock drag, a geometry similar to the Type 4735 gauge, but incorporating a Biconvex cross section with a t/c ratio of 37.5% was hypothesized, andit was assumed that the flow would go supersonic at some point in the temperature-velocity regime.

The projected area was estimated at 1.547×10^{-3} ft.^{2} at 1.8 inches immersion depth. The ratio of specific heats of the medium at 1.3, and a value of 58 was given 2K. Density, taken at 0.56×10^{-3}, at ambient, was corrected for the discrete temperatures of 773°K, 1273°K, 1773°K, 2273°K and 3273°K, selected for the estimate. Velocities of 2000, 3000, 4000, and 5000 ft/sec were likewise used. Results of the computations were plotted, using a modified "carpet" technique, and are shown in Figure 2.

It is emphasized that, since values selected for the various parameters were not necessarily those to be actually encountered in use, no significance can be placed on any data point in the carpet. However, the graph does indicate that, depending upon the combination of temperature and velocity attained at light-off, and during the short time internal thereafter, until stability is reached, there is a possibility of an extremely large load "spike" occurring for a brief period of time, and a consequent catastrophic failure in the immersed member, if loaded transversely. The existance of such "spikes" in other tests has been suspected for some time. No other reasonable explanation has been advanced for random, dramatic failures of probes being tested in various engines and gas generators. Such failures have been invariably associated with fuel-rich starts and/or unstable burning. That events in the sequence of ignition and combustion happen in very short time intervals is well known;

viz: the pressure rise of 250,000 psi/sec, and the suspected presence of a short duration, very high temperature spike in a current, large reaction motor.

The two estimates of dynamic loading given above are not based upon actual operating parameters. It is felt however, that the shock drag may present a problem worthy of consideration, if only because of the relative magnitude of the forces developed. Therefore, any future designs will include provision for minimizing the reaction to such forces, within limits imposed by the geometry of the installation.

3.2 Oxidation Resistant Coatings

Early in this program, it was realized that a serious problem existed in retarding oxidation of Tungsten. At the time, the state-of-the-art was not well known. This area of endeavor, consequently, has received a great deal of attention. An extensive review of published literature has been made and the results of the search tabulated. (see Table I) Only data that has been substantiated by test is reproduced in the table. Earlier tests at ACL of such materials, claimed by the manufacturer to have a protective quality at temperatures over 3000°F, were disappointing in the extreme.

TABLE I

SUMMARY OF OXIDATION RESISTANT COATINGS

COATING	MFR	MIL THKNS	°F MAX TEMP	HRS LIFE	TESTED BY
Pt	AMF	5	3000	5	AMF
Diffusion (Undentified)	AMF	U U	2800 3200	10 3-4	AMF
W-2	Chromalloy	U	2700	60	Chromalloy
Si	G T & E	3-4	3300	0 — 10	G T & E
Si-A	G T & E	3-4	3300	— 10	G T & E
Si-B	G T & E	2	3300	— 10	G T & E
Oxides (ZrO_2, ThO_2, BeO, HfO_2)	LMSC	10-30	3992	1 min. Failure by Oxidation	LMSC
Boron Nitride (Pyrolytic)	A.D.Little	U	3272	U	A.D.Little
Durak MGF	Chromizing Crop.	U	4600	10 min.	U
$Ta-HfO_2 50ThO_2$	Harvey Aluminum	30	5000	U	U
Cr-ZrB	Value Engrg.	U	4000	35 min.	Redstone Arsenal
Silicide, Unmodified	G T & T	3	3272	11-16	G T & T
Silicide # 1 Modified	G T & T	3	3272	19-26	G T & T
Silicide # 2 Modified	G T & T	3	3272	20	G T & T
Sn-Al -	G T & T	U	2000	8	
Binary Aluminide	Republic Aviation	U	3500	2.5	Republic Aviation

NOTE: U indicates unknown

3.2 Oxidation Resistant Coatings Cont....

In researching the reports from which the data in Table I was taken, it became apparent that very little had been done toward taking data at temperatures above 4000°F, probably because the research programs were oriented toward long term oxidation resistance for structures at re-entry temperatures, rather than short term resistance for components, at higher temperatures.

In other work reviewed, the degradation of silicide coatings at oxygen pressures from .1-760mm was studied by LMSC. In high velocity, low pressure air, a particular coating had a life of 2 hours, at 2700°F, but at one atmosphere, it lasted 15 hours. The failure mechanism appeared to be related to the evaporation of SO under high temperature, low pressure conditions. The lowest oxygen pressure at which the SO_2 film appears to be stable is 5mm O_2.

LMSC also investigated coatings for re-entry bodies at 3000°F to 4500°F. Their recommendation was for spray-coating of the W substrate with non-reactive oxides, using the oxide as a barrier to high velocity air, to reduce oxygen pressure at the substrate surface to a level such that oxidation rate is not a serious short term consideration. Tests of this technique at 3000°F and 5mm O_2 resulted in an increase in life in high velocity air from 8 minutes with uncoated Mo to 30 minutes with a 10 mil coating of ZrO_2.

Many researchers exhibited interest in a composite of refractory carbides and Tungsten. Typical of these is TaC-W. Aerojet-General reports that reaction between these two materials occurred after 2 minutes at 5400°F. General telephone reported that eutectic formation occurs as low as 5160°F. Allison Division, G.M.C. reports the reaction temperature of W-TaC at 4980°F.

The consensus of the research groups seems to be that the coating exhibiting the most promising characteristics for short term use at temperature levels above 3000°F are modified disilicides, composites, and thin coatings of high refractory, non-reactive oxides.

3.3 High Temperature Reaction: Oxides, Nitrides and Carbides vs Tungsten

One of the tasks imposed in this contract is to investigate "the reaction of oxide coatings with Tungsten in relation to the emf output". This investigation has been in progress since the increption of the contact.

In comparing results obtained by various researches, Table II is presented incorporating data, not only regarding the oxides, but other materials as well.

TABLE II

REACTION OF TUNGSTEN WITH OXIDES, NITRIDES AND CARBIDES AT ELEVATED TEMPERATURES

Material	Reaction
ThO_2	No reaction at 5430°F
ZrO_2	No reaction at 5430°F
BeO	No reactive to 4200°F
MgO	Entirely reacted at 4530°F
UO_2	Not reactive at 5430°F
Al_2O_3	Vaporizing, but no other reaction at 5430°F
Y_2O_3	No reaction at 5430°F
HfO_2	Slight interdiffusion at 5240°F
TiN	Slight reaction at 5240°F
ZrN	Severe interface irregularities at 5430°F
TaC	W-TaC eutectic melted at 5160°F
HfC	W-HfC eutectic melts about 5070°F
ZrC	W-ZrC eutectic melts below 4890°F
(Ta-20Hf)C	W-(Ta-20Hf)C eutectic melts below 4890°F

3.3 High Temperature Reaction Oxides, Nitrides and Carbides vs Tungsten Cont....

The work resulting in most of the information in Table II was performed by General Telephone Electronics Labs. Others agree essentially with their results.

The consensus seems to be that the refractory oxides, with the exception of MgO, are generally unreactive with Tungsten.

The refractory carbides and nitrides would be of little use as coatings on Tungsten at temperatures above the melting points of the eutectics, or at temperatures near those at which reaction was noted. It can thus be stated in general that above 5000°F the oxides are indicated, but that some carbides and nitrides would be of use below 5000°F.

The tests were run on Tungsten foil which, having been mechanically worked, probably exhibits a grain structure much larger than the electro-chemically formed sheaths of the Type 4735 gauges. Therefore, the interactions, particularly those associated with diffusion, may be quite different. The data, in Table II, being essentially qualitative in nature, does not establish working ranges for the materials, but does serve as a basis upon which to predicate directed effort.

The effect of reactions of Tungsten with the oxides on the emf output of the gauge is not necessarily a straight forward function of temperature. From Table II it could be inferred that the non-reactive refractory oxides could be used with impunity to temperatures well above 5000°F. The effect however may occur in mechanisms other than those of chemical reaction. Used on the exterior of the gauge, thoria, zirconia, yttria and hafnia would not react. If they were not applied uniformly, however, the heating rate through the coating would be different and an error in output could result. If the coating thickness was too great, cracking and separation could occur, resulting in errors due to non-uniform radiative and conductive losses, as well as losses due to melting of the resultant oxides of tungsten. Used internally, as electrical insulators, the oxides

3.3 High Temperature Reaction Oxides, Nitrides and Carbides vs Tungsten Cont....

would perform like those used externally, except that there would be less effect of local increases of temperature due to stagnation of the medium. The greatest errors are more likely to occur because of the increase in electrical conductivity associated, in these materials, with high temperatures. Although there is some disagreement among researchers as to the changes in electrical conductivity, the consensus seems to be that the zirconia, hafnia and yttria, although more refractory than beryllia, become conductive at a lower temperature. Little information is available concerning Uranium Oxide in this regard.

3.4 Electrical Insulation

Since the time of the last report, conferences have been held with two other researchers working in the field of high temperature electrical insulators. Both report little success in finding a suitable material, and are presently directing their efforts toward designing for no insulation. ACL is continuing effort in this area, with present thinking directed toward gas dielectrics.

3.5 Requests for Information

It is requested that the information set forth in Para. 3.1.8 of ACL Report No. T-1097-5 be given early attention, in order that design of the second generation prototypes may be continued without delay. It is also requested that ACL be furnished with any available results of test of the first three prototypes delivered.

3.6 Current Tests

The tests of lead wires and coatings are continuing, but had not reached completion at the time of this report.

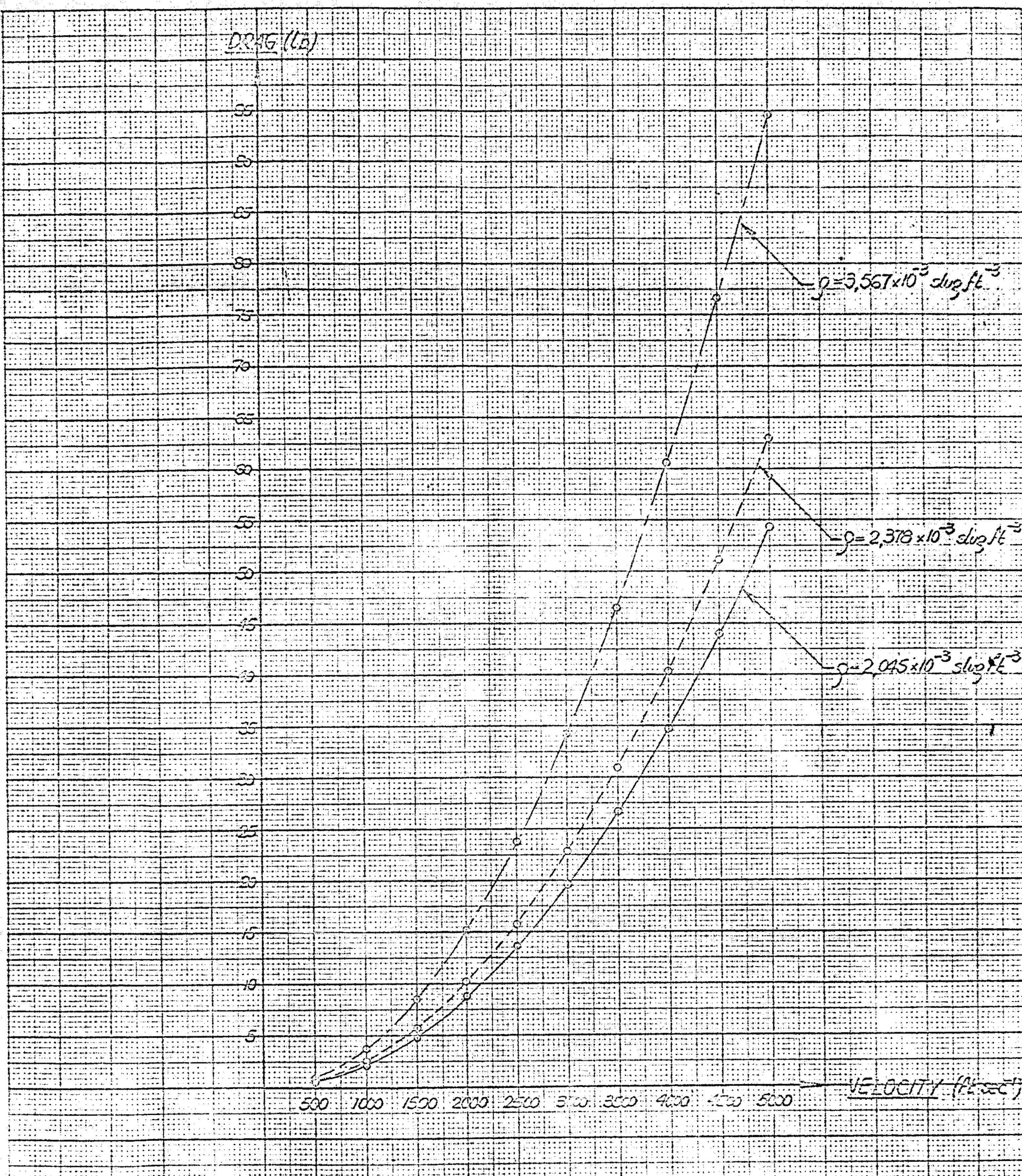

FIGURE 1

FORM DRAG

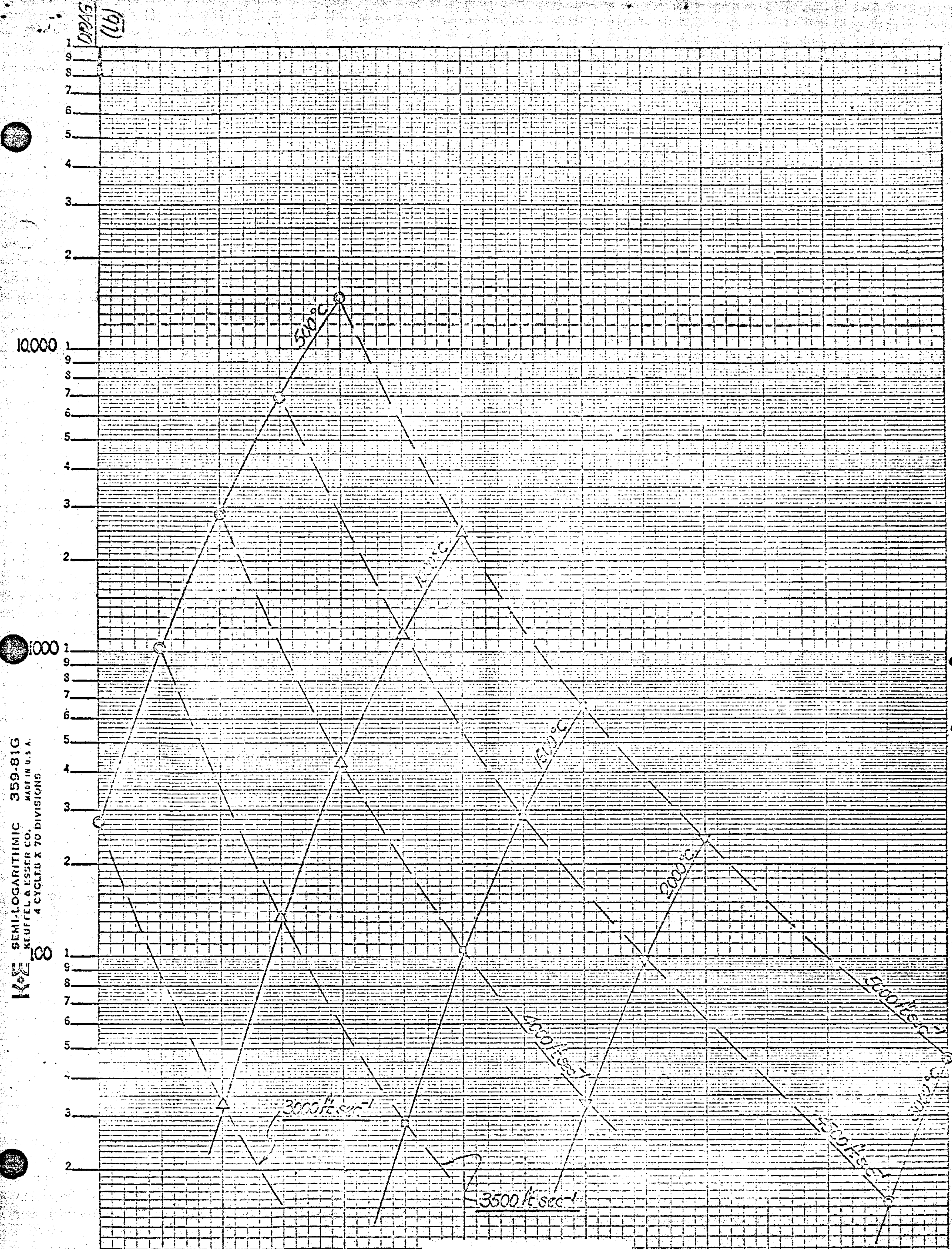

FIGURE 2

SHOCK DRAG

SECTION IV

PROGRAM FOR NEXT INTERVAL

4.0 Objectives for the interval 1 December 1963 to 1 January 1963.

a. Continue calibrations and oxidation tests.

b. Continue lead wire tests.

c. Continue search for insulators.

d. Continue design of second generation gauges.

SECTION V

STATEMENT OF MAN HOURS

5.0 Hours by Category

Category	Previous Periods	Current Period	To Date
Engineering	442.00	33.50	475.50
Clerical	70.50	38.50	109.00
Fabrication	535.00	47.00	582.00
Consulting	5.50	10.00	15.50
Drafting	32.00	19.00	51.00